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Effects of Backbone Disorder on Electronic Transport in DNA Molecules

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ABSTRACT

Static disorder of DNA backbones exists in electronic transport measurements of DNA molecules. We propose a model to examine the effects of the backbone disorder on electronic transport in DNA. The model is based on a tight-binding Hamiltonian with periodic overlapping π orbitals of base pairs coupled to disordered backbones. The dynamical behaviors of electrons are demonstrated in a framework of quantum dynamics. We show that the localization length of electrons undergoes a sharp transition as the disorder strength increases, namely, it decreases in the regime of weak disorder but increases in the regime of strong disorder. Our finding provides a new understanding of the diverse experimental results of the electrical conductivity of DNA molecules.

Keywords: DNA; electronic transport; backbone disorder; localization; molecular electronics.

1 INTRODUCTION

Electronic transport in DNA molecules has attracted considerable interests in recent years [1-26]. A clear understanding of the nature of electronic motion in DNA is of vital importance for the research of a wide range of important biological processes such as repair of damaged bonds in cells and detection of mutations [1-6]. Moreover, DNA molecules of controllable conductivities may provide a new set of building blocks for the cutting-edge molecular electronics [7-26]. However, in spite of tremendous experimental efforts [7-18], the fundamental question whether the DNA molecule is an electrical conductor or not remains controversial.

Experimental measurements showed diverse results of electrical conductivity of DNA molecules. Individual λ-DNA molecules were reported to be insulating [7,8], metallic [9], and super-conducting [10]. A variety of theoretical models [19-26] have been proposed to understand the diverse experimental observations but none of these models provides a complete interpretation of the whole phenomena. It is widely believed that the effective overlap of π orbitals of adjacent base pairs provides pathways for electrons in DNA. As a consequence, electron motion in a DNA molecule is sensitive to its sequence order of the base pairs. A λ-DNA molecule has a disordered base-pair sequence. Density functional theory (DFT) calculation indicates that a λ-DNA molecule of eleven base pairs are insulating [8]. Though DFT calculation is able to provide accurate results for short DNA molecules under idea conditions, it is lacking capability in predicting transport properties for long DNA molecules, in particular when there are disorder and interactions between the DNA and environment. It is very important to develop phenomenological models for understanding the transport properties of DNA molecules. Recently, a study based on a single-band tight-binding model of λ-DNA molecules show that whether or not λ-DNA is conducting strongly depends on the correlation of its disordered base pairs [19]. Electrons display a metal-insulator transition behavior in a λ-DNA with correlated base pairs. This finding may shed new light on understanding the experimental results of the transport properties of λ-DNA molecules.

Double-stranded poly(G)-poly(C) DNA is a comparably simpler molecule with periodic G-C pairs. However, even for this system, the underlying mechanism of the electron transport is far from being understood. The first experiment [13] showed that a poly(G)-poly(C) DNA molecule of 10.4nm long displays wide-band-gap semi-conductor behavior. Later, another experiment showed that the semi-conductor behavior holds up to 100nm scale [14]. However, more recently, experiments found that poly(G)-poly(C) DNA molecules are insulating at length scales longer than 40nm [15]. Temperature dependence of *I-V* curves for poly(G)-poly(C) DNA molecules of 20nm long was systematically investigated recently [16]. It was shown that most experimental results except the temperature dependence of the hopping distance can be interpreted within the polaron hopping model [16]. Moreover, experiments showed that the conductivity of DNA molecules is very sensitive to measurement environment and doping [12,17,18]. Slightly increasing the relative humidity largely enhances the DNA conductivity [12,17]. The conductance of poly(G)-poly(C) DNA can be easily controlled by several orders of magnitudes increase using oxygen doping [18].

For the poly(G)-poly(C) DNA molecules, one expects that the periodic overlapping of π orbitals of G-C pairs would form conduction bands supporting metallic or semiconducting behaviors. Considering the difference between the theoretical expectation and the diverse experimental observations, we believe that disorder in DNA play a significant role in controlling the conductivity of the poly(G)-poly(C) DNA. DNA has a special double-helix structure with base pairs attached to two sugar-phosphate backbones. The backbones wind around the helix axis and the bases are on the inside of the helix with a spacing 0.34nm. Due to the unique structure of DNA, the backbones are much easier to be disturbed than the bases. For instance, for a DNA molecule lying on a substrate, the backbones contact with the substrate and the binding of surface atoms with backbones may change the local structures of the deoxyribose sugar and the phosphate, resulting in backbone disorder. This is more severe when the substrate surface is not smooth. In the case of interaction of DNA with molecules such as H_2O and O_2, it is difficult for these molecules to penetrate into DNA because of their relatively large sizes. Thus, most probably these molecules just attach to the backbones or its neighboring sites, inducing strong backbone disorder. Backbone disorder can be also induced by chemical, electrical, and mechanical treatments in manipulation of DNA for construction of DNA bridges for current measurement. In addition, the sugar and phosphate molecules of the backbones are expected to have larger thermal fluctuations than the bases because of their looser structures. From this analysis, we believe that the backbone disorder have significant influence on the electron motion in DNA. In this paper, we propose a tight-binding model to examine the effects of the backbone disorder on electronic transport in poly(G)-poly(C) DNA molecules.

2 MODEL

Our model is based on the three-band tight-binding model, which was originally proposed to explain the *I-V* curve of the poly(G)-poly(C) DNA molecule of length 10.4nm [26]. The DNA structure and the corresponding model are schematically shown in Fig. 1. In Fig. 1, *b* sites represent G bases, and the sites marked by c_+ and c_- account for the upper sugar group sites and, possibly, for the C bases with the relative lower strand sites. The Hamiltonian is given by

$$H = \sum_n \varepsilon(n)\left|n\right\rangle\left\langle n\right| + \sum_{n,n'} h(n,n')\left|n\right\rangle\left\langle n'\right|,$$

where $\varepsilon(n)$ is the on-site potential, and $h(n,n')$ are the nearest-neighbor hopping integrals. For *b* sites, $\varepsilon(n) = \varepsilon_b$ and $h(n,n') = h_b$. The on-site potential for a c_{n+} (c_{n-}) site is ε_{n+} (ε_{n-}). The hopping integral between a c_{n+} (c_{n-}) site and *b* site is h_+ (h_-). In [26], $\varepsilon_{n\alpha}(\alpha = \pm)$ is a constant independent of site position. In our study, we consider the backbone disorder by introducing a random distribution of the on-site potentials for the backbone sites, namely, $\varepsilon_{n\alpha}(\alpha = \pm)$ is chosen randomly within the interval $[-W, W]$.

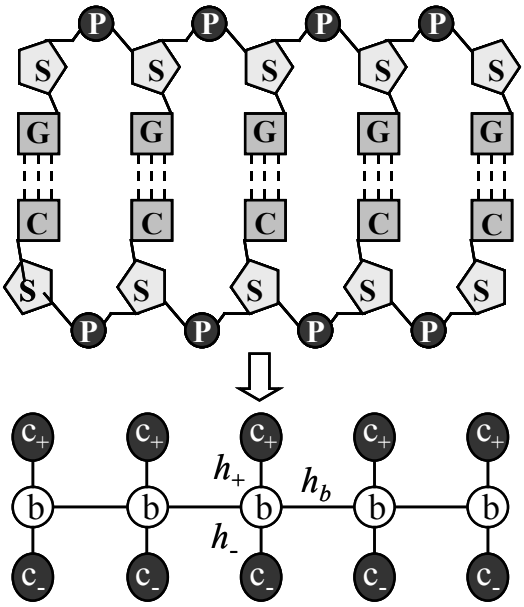

Figure 1: Schematic presentation of a poly(G)-poly(C) DNA molecule and the corresponding tight-binding Hamiltonian model.

3 QUANTUM DYNAMICS IN DNA

In order to unveil the intrinsic behavior of electronic motion in DNA molecules with backbone disorder, we study the dynamics of electrons in a long DNA chain. Electrons are initially located at a site position $\vec{r}_0$. The dynamics of electrons is governed by the Schödinger equation, which for the tight-binding models has the form

$$i\frac{\partial}{\partial t}\psi(n,t) = \varepsilon(n)\psi(n,t) + \sum_{n'} h(n,n')\psi(n',t)$$

with initial condition $\psi\left(n, t=0\right) = \delta_{n,0}$, where $\psi(n,t)$ is the wave function amplitude at position $\vec{r}_n$ at time *t*. The dynamical behavior of electrons is described [27,28] by the mean square displacement $r(t)$ defined as

$$d(t)=\sqrt{\sum_n \left|\vec{r}_n-\vec{r}_0\right|^2 \left|\psi\left(\vec{r}_n,t\right)\right|^2}\ .$$

We note that, three typical behaviors, namely, the ballistic motion, diffusion, and localization correspond to $d(t)\sim t$, $\sim\sqrt{t}$, and $\sim t^0$, respectively.

In our calculations, we consider poly(G)-poly(C) DNA molecules of 301 G bases. Electrons are initially located at the central *b* site of each DNA molecule. Hamiltonian parameters are taken from [26], which were obtained by fitting the experimental data of *I-V* curves. Specifically, $\varepsilon_b=0$, $h_b=0.37$ eV, and $h_+=h_-=0.74$ eV. Different from [26], $\varepsilon_{n\alpha}(\alpha=\pm)$ in our calculations takes random values within the interval $[-W,W]$ in unit of eV.

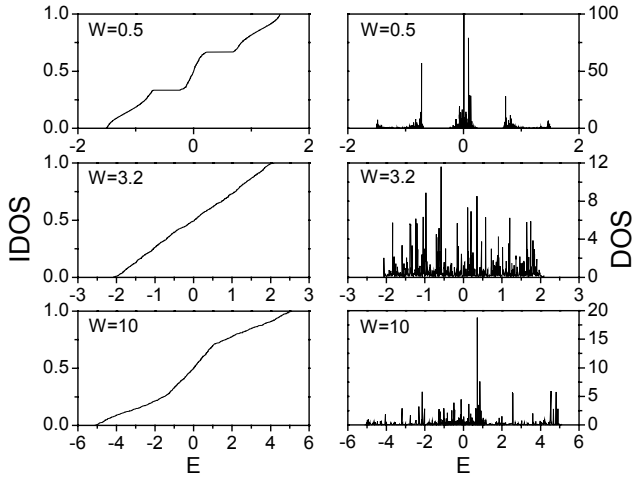

Figure 2: Electronic integrated density of state (IDOS) and density of states (DOS) of a DNA molecule with different backbone disorder strength *W*.

Fig. 2 illustrates the integrated density of states (IDOS) and the density of states (DOS) of a DNA molecule with different degree of backbone disorder. As shown in [26], the spectrum of a perfect DNA with $W=0$ has a gap centered at $E=0$. From Fig. 1, we can see that additional states occur in the central region of the gap when there exists disorder. The number of these gap-states increases as W increases. No distinguishable gaps exist in the spectrum once W exceeds a critical value. In addition, the DOS is very spiky when disorder exists, implying the localization of eigen-states.

Fig. 3 shows the mean square displacement $d(t)$ as a function of time *t* for an electron in a DNA molecule with different backbone disorder. For $W=0$, we find a ballistic motion with $d(t)\sim t$, as expected for periodic systems. For DNA molecules with finite backbone disorder, we find that $d(t)$ first increases with time but become flat as time goes to large. This indicates that the electron is localized in a certain region of the DNA due to the existence of the backbone disorder. The long time limit of $d(t)$ gives a localization length, $L(W)$, which defines the degree of spatial confinement of electrons under backbone disorder *W*. The observed confinement of electrons is in consistent with the general theory of Anderson model of disorder, which predicts that any amount of disorder in one-dimensional systems leads to localization of electrons.

We note that a well-established view about the disorder-induced electronic localization is that localization length decreases as disorder strength increases. Our results for the DNA molecules with backbone disorder show a quite different behavior from the traditional view. As shown in Fig. 2, there exists a transition with a well-defined critical value $W_0=3.2$. In the regime of $W<W_0$, $L(W)$ decreases as W approaches to W_0. However, in the regime of $W>W_0$, $L(W)$ increases as W increases, indicating that strong backbone disorder can enhance the mobility of electrons in DNA.

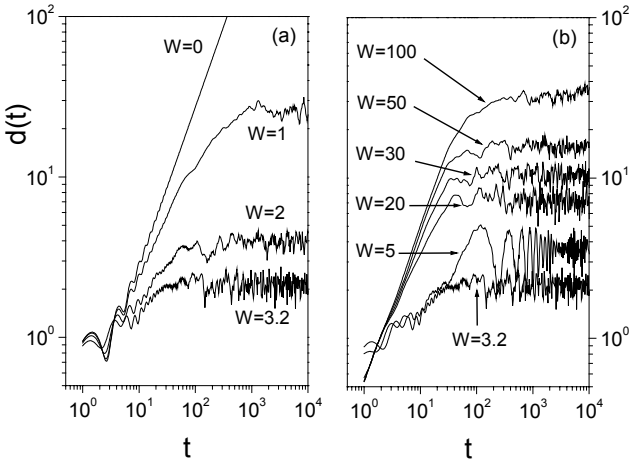

Figure 3: Mean square displacement *d* as a function of time *t* for DNA molecules with different amounts of backbone disorder.

4 DISCUSSIONS AND CONCLUSIONS

The unique behavior of electronic localization in DNA molecules with backbone disorder provides a new understanding to the recent diverse experimental observations of the conductivity of poly(G)-poly(C) DNA molecules.

For transport measurement in a dry environment (vacuum), the backbone disorder is induced mainly by the

interaction between DNA and substrates, and by the mechanical and electronic treatment of the DNA for creating bridges. In this case, the backbone disorder is expected to be relatively small and the localization be described by the behavior in the regime of small disorder. From Fig. 3(a), one can see that, quite different transport properties are expected depending on the disorder strength. For $W << W_0$, $L(W)$ can be very large reaching thousands of bases, indicating that the DNA molecule can be a good conductor at length scale of hundreds of nanometers. If W is relatively large close to W_0, $L(W)$ can be as small as several bases. In this case, the DNA molecule is a good conductor only at the length scale of several nanometers.

It has been shown that the higher the humidity in the transport measurement the higher the conductivity of DNA [12, 17]. There exists strong backbone disorder when the relative humidity is high because of the interaction of DNA molecules with water and ions in the water. Thus the localization length in this situation is expected to be described by the behavior in the regime of strong disorder, which predicts that the stronger the disorder the better the conduction. This prediction is in consistent with the experimental results.

Recent experiments also showed that doping O_2 [18] into DNA greatly enhances the conductivity of poly(G)-poly(C) DNA. This result was attributed to the increase of carrier density [18]. DNA is a one-dimensional system. Under the view of traditional electronic theory of disorder, doping simultaneously induces localization of carriers as it increases the carrier density. Therefore, the increase of carrier density itself cannot explain the drastic increase of the conductivity as observed in experiments. On the basis of our finding, the intriguing phenomenon can be well explained under the assumption that the doping only induces strong disorder of the DNA backbones. In this case, the doping not only increases the carrier density but also greatly increases the localization length of electrons. These two factors can result in significant increase of the conductivity. Further experiments to probe the absorption sites of the doping materials are very helpful in confirming our theory.

In conclusion, we show that backbone disorder of DNA molecules has a unique influence on the electronic transport in DNA. We find that the localization length of electrons undergoes a sharp transition as the disorder strength increases, namely, it decreases in the regime of weak disorder but increases in the regime of strong disorder. Our finding provides a new understanding of the diverse experimental results of the electrical conductivity of DNA molecules.

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